

AUTHIGENIC CARBONATES IN QUATERNARY SEDIMENTS AND SOILS AND RELATED GEOCHEMICAL SYSTEMS OF DANUBE LOWLAND (SW SLOVAKIA) II.

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Citation: Čurlík, J., Kromka, M. (2023). Authigenic carbonates in Quaternary sediments and soils and related geochemical systems of Danube Lowland (SW Slovakia) II. *Pedosphere Research*, vol. 3, no. 1, pp. 43–62. NPPC – VÚPOP 2023. ISSN 2729-8728.

Abstract

We present a framework for interpreting the carbonate geochemical systems in sediments and soils of Danube Lowland (SW Slovakia). The term carbonate geochemical systems we refer to the supergene systems in which carbonate authigenesis is the dominant factor of their formation. Presented article gives an overview of the sources of calcium and models of authigenic carbonates formation that have been proposed in literature, including presenting our new landscape-geochemical model. Study is referring to the morphological classification of authigenic carbonates, mineralogical classification – calcretes, as well as other issues concerned to the Danube Lowland. Carbonate authigenesis is epigenetic geochemical process which leads to the excretion (neof ormation) of carbonates in host sediments and soils independent on their genesis. In more details are described related supergene carbonate geochemical systems in Danube Lowland (SW Slovakia) – loesses and fluvial sediments including their history.

Keywords: carbonate authigenesis, geochemical landscape system, loess, alluvial sediments, Danube Lowland

INTRODUCTION

In the first section of our contribution published in Čurlík & Kromka (2022) more space was devoted to the critical reviewing of terminology, nomenclature, and classification of authigenic carbonates. In this (continuing) paper more attention is paid to the sources of calcium, models of authigenic carbonates formation, in historical context. Attention is paid to the description of individual subsystems in Danube Lowland (SW Slovakia) – loesses and fluvial deposits. Carbonate geochemical systems of the supergene zone differ from the other geochemical systems by the concentration of calcium, and by the presence of the paragenetic association of elements which are bound to authigenic carbonates in the host materials. Despite the different genesis of the two main subsystems, their common feature is the preservation of the carbonate nature of the host rocks and soils. We present a framework for interpreting carbonate character of all Danube Lowland. However, pedogenesis influenced the redistribution of carbonates and caused geochemical zonality in soils, but carbonate character the whole landscape remains. Carbonate character the Danube Lowland is preserved due to evapo-transpiration water regime of the region, many sources calcium, including those brought by fluvial activities of lowland rivers. We stress that authigenic carbonates produced in soils and sediments during early diagenesis, has played a big role in the carbon cycle.

MATERIALS AND METHODS

Samples of more than 400 soil profiles from the loess hills of the Danube Lowland (Trnavská, Nitrianska, Žitavská and Hronská pahokatina loess hills) were evaluated and 173 soil profiles from region of Žitný

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ostrov (Danube lowland). Selected chemical analyses (main and trace elements – Ca, Mg, K, Na, Cu, Fe, Sr) from the A and C soil horizons were evaluated in order to comment on: behaviour of elements during pedogenesis and understanding of soil zonality. The basic soil parameters (pH, CaCO₃ content, texture) were analyzed. Based on large number of analytical data and statistics geochemical maps were constructed to understand the distribution of elements in soils on loess and on alluvial sediments of the Žitný ostrov. The subject of study was supplemented by micromorphological observations of selected soil profiles according to the methodology (Stoops *et al.* 2003, Stoops *et al.* 2010). Some published works were also used for comparison of the first author (Čurlík 1985, Čurlík & Mejeed 1996). The samples were taken as part of the Geochemical Atlas of SR (Čurlík & Šefčík 1999). Sampling of loess and alluvial sediments was done using drilled probe from a depth of 120–150 cm. The analyses were carried out in the Ecological laboratories Ltd. Spišská Nová Ves by the methods of atomic absorption spectrometry. Analytical procedures are described in more detail, in the work of Čurlík & Šefčík (1999). From the acquired database, data for loess and alluvial areas were selected, and from them corresponding geochemical maps were constructed.

Morphological classification of authigenic carbonates

It is based on the visible signs that can be describe directly in the field. They are needle shaped, powdery, nodular, pisolitic, tubular, laminar, honeycomb, layered, conglomeratic and others (Čurlík 1993, Chen *et al.* 2002, Stoops *et al.* 2010, and others). *Powdery* forms are fine (micritic), usually friable, dispersed, or clustered in the soil matrix. *Nodular* carbonates are composed of discrete, friable to solid, irregular (nodular) forms. Their size, shape, degree consolidation and the content of CaCO₃ in nodules, as well as their purity is variable. *Carbonate clusters* are formed by precipitation in the pores and then expanded into the matrix. *Pisolitic* forms are similar to nodular, but they are concentric and have a regular isometric shape. *Tubular*, rhizo-concretionary forms are developed most often around former roots, channel-like pores, and cavities. Their size is very variable and can reach up to several tens of cm, in the case excretion from groundwater. Development various features such as nodules, pedotubules (tubes), clusters, relate to processes of dissolution, leaching and recrystallization (Klappa 1980, Semeniuk & Meagher 1981, Wright *et al.* 1995, Čurlík & Mejeed 1996, Chen *et al.* 2002). *Laminar* forms occur in places where powerful positions of calcretes are present, which they did not undergo significant pedogenic modification.

The main process of their creation is plant root activity (e.g., Wright *et al.* 1995). Layered, conglomeratic and boulder forms were also described by Alonso & Zarza (2010). Hardpan (hardpan calcrete) is a designation for continuous layers of solid cemented authigenic carbonates in the host materials that have a micritic microstructure. They were studied in Žitný ostrov area (Čurlík & Mejeed 1996).

The majority of authigenic carbonates is a mixture of several morphological, or transitional types, but their detailed classification is not processed. From petrological point of view, the authigenic carbonates are formed by needle-shape, micritic and micro-sparitic calcites (Čurlík & Meejed 1996, Čurlík & Kromka 2022) (Fig. 1).

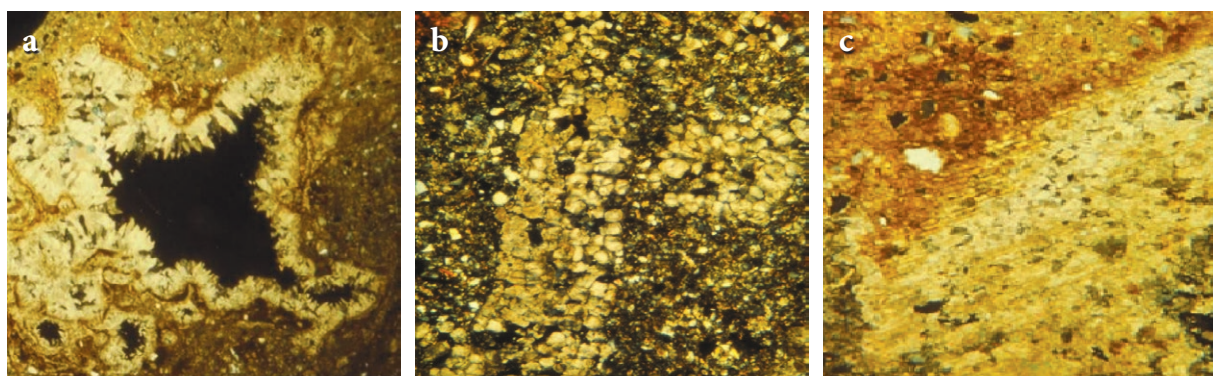


Figure 1. Calcified plant remnants in loess, a) micro-sparitic domains in plant roots, b) calcified (micritic) plant tissue. Note recalculated micro-sparitic domains in the middle of the picture (cross polarisers).

Mineralogical classification of authigenic carbonates – calcretes

Authigenic carbonates (calcretes) were mineralogically classified by Nettenberg (1980) based on the percentual ratio of two basic minerals namely calcite and dolomite:

Calcretes 2% (approx. eq. of MgCO_3 in %)

Magnesian calcretes 2–5%

Dolomitic calcretes 5–25%

Calcitic dolocretes 25–40%

Dolocretes >40%

The results of our studies show that the dominant mineral in the authigenic carbonates of the Danube Lowland (SW Slovakia) is *low-magnesium calcite*. We also recorded the co-occurrence of dolomite, but its authigenic origin has not been reliably proven. Dolomite, which weathers powdery, is less dissolving than calcite. It is possible that clastogene powdery dolomite is incorporated into the matrix of authigenic calcites, which makes its X-ray study difficult (Čurlík 1993, Čurlík & Mejeed 1996). According to data from the literature, stoichiometric dolomite under similar conditions it does not even form (Degens 1965, Folk 1974) and data on the content of dolomite refers to *the protodolomite*, which contains up to 10 mol % more CaCO_3 than dolomite. Under the microscope some acicular aragonite-like forms were observed on Žitný ostrov area, but X-ray analyses confirmed only the presence of calcite. Because it is known that aragonite it does not remain in sediments for long and recrystallizes to calcite as it ages (Khadikar *et al.* 1998, Lasemi & Sandberg 1984) probably those are paramorphoses after aragonite. Several other types of carbonates were also described in the literature (siderite, high-magnesium-calcite).

Sources of calcium (necessary) for authigenic carbonates formation

For the formation of carbonates in general, calcium sources, suitable climatic conditions and time are necessary. Sources of calcium and other ions (Mg, K, P, Na, Sr, etc.) necessary for the formation of authigenic carbonates can be both, *abiogenic and biogenic* (Capo & Chadwick 1999, Čurlík 1985, Čurlík 1993, Aristovskaja 1980).

Among the most important sources belong:

- *Aeolian dust* of the arid regions (+ aerosols) may primarily contain a certain proportion of carbonates. It can be wind-blown from beaches and dunes, from drying salt lakes, from alluvial sediments and from the surface of soils of arid areas with sparse cover vegetation (Milnes & Hutton 1983). Because the contribution of dust particles is subject to temporal fluctuations during the Pleistocene, a much higher aeolian Ca contribution is associated with cool and dry conditions of glacial periods in the past.
- *Precipitation* is considered as more important source of Ca than aeolian dust (Gile *et al.* 1966, 1981, Hill *et al.* 1999, Monger 2002). Chemical analyses of precipitation showed that carbonates formed from precipitation can exceed two to three times the amount that came from dust-borne carbonates in the atmosphere. The influence of sea waters on carbonate precipitation is only stronger near the coast (Hutton & Leslie 1958).
- *Mineralized (soil-) and groundwaters* are responsible for the formation of carbonates in alluvial drainage systems, including coastal zones and former aquifers (e.g., Carlisle *et al.* 1983, Semeniuk & Meagher 1981, Sobecki & Wilding 1983). Water is transport medium of ions. Their concentration in groundwater increases by passing through solid phases of water-bearing strata, as a result of gradual water evaporation in the capillary zone (evaporative concentration of elements), in places where evapotranspiration water regime is created in soils. Groundwater of arid regions often contain up to 1% of dissolved Ca and CO_2 compared to 0.036% in the atmosphere (Monger 2002).
- *Plants* can have unexpected consequences on calcite accumulation and on the overall calcium balance in the soil. Their above – and underground parts contain Ca-oxalates and calcite neoformations. Decomposition of Ca-oxalates in the soil may not proceed to basic components, but depending on conditions, they are slowly transformed into authigenic carbonates (Monger 2002, Verrecchia & Verrecchia 1994, Čurlík *et al.* 2011, Martin *et al.* 2012, Cailleau *et al.* 2014). Decomposing organic mat-

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ter, shells and skeletons of animals accumulate in soil. They are sources of Ca and CO₂ ions for the formation of carbonates. It is documented that the increase in Ca contents in the soil environment is also reflected in increased contents of Ca-oxalates in plant tissues (Franceschi & Nakata 2011).

- *Transfer of Ca* in the landscape from sources rich in Ca, by the movement of soil and groundwater (Ca, HCO₃ ions in solution), or by mechanical erosion and transfer of clastogene forms of CaCO₃.
- *Abiotic and biotic dissolution* (weathering) of clastogene carbonates and silicate minerals (Capo & Chadwick 1999, Čurlík 1985).

From the stated, it is evident that sources of calcium for the formation of authigenic carbonates in cover sediments and soils are many. Permanently available source is precipitation. Maybe with it is necessary to count in places where carbonates are formed mainly under the influence of groundwater. During the formation of authigenic carbonates, several sources of Ca²⁺ and Mg²⁺ can be available (e.g., Alonzo-Zarza & Wright 2010).

Review of existing and a new proposed model of authigenic carbonates formation

Authigenic carbonates, mainly calcite and dolomite, are formed in seas and oceans, in estuaries, lakes, rivers, caves, springs, cover sediments (loesses, fluvial sediments), weathering crusts and in soils (e.g., Warren 1983, Amiel 1975). If we omit the geological (biogeochemical) processes of carbonates formation in the seas and oceans, we can, regarding the mentioned sources of Ca, connect the formation of authigenic carbonates with the *downward, upward and lateral* (horizontal) movement of water saturated in relation to calcite (Gile *et al.* 1966, Monger 2002). The movement of water plays a very significant but different role in each landscape position. This is also the reason why there is no uniform genetic classification that would take into account hydrological conditions in the formation of authigenic carbonates. In accordance with the knowledge of the mentioned sources of Ca and the movement of water in the landscapes, Monger (2002) summarized four groups of carbonate formation models: (a) *per descendum* (b) *per ascendum*, (c) *in situ*, and (d) *biogenic* model. They refer to the various hydrological and hydrogeological conditions found in surface and soil water, gravity-, capillary- and groundwater (in the phreatic zone) (Carlisle 1983).

a) *Per descendum* model explains the formation of carbonates by downward movement of precipitation (meteoric) waters (Gile *et al.* 1966, Li *et al.* 2018). By this movement, the carbonates present in the upper part dissolve and subsequently precipitate from the solutions in lower positions, after the water leaks out. Three different sub-models could be distinguished: *first model* if carbonates (clastogene or authigene) are present in the host sediments no addition of calcium is necessary. In this case upper depleted – and lower, in carbonates-enriched horizons (eluvial-illuvial processes) are formed. The *second sub-model* is applied when soils (sediments) develop on non-carbonate substrates. Then the addition of Ca²⁺ or carbonates to the system through the atmosphere (precipitation water, dust) is necessary. *The third case* occurs when, in addition to the downward movement, there is also a lateral movement of aqueous solutions, which is the most common phenomenon in slope conditions. Precipitation of carbonates occurs just below the surface in the case of an arid climate. From this idea comes the opinion that the depth of occurrence of authigenic carbonates is a function of climate and time and can be used as a paleo-indicator of climatic changes. Evaporative concentration of elements in the capillary (vadose) zone of rivers plays an important role (Butt *et al.* 1977, Semeniuk & Meagher 1981, Carlisle *et al.* 1978, 1983).

b) *Per ascendum model* is based on idea of the upward (ascendant) movement of capillary waters. Groundwater is a transport medium for ions necessary for the formation of carbonates (Ca²⁺, Mg²⁺ and CO₃²⁻). Shallow ground- and pore waters participate in the redistribution of carbonates. Their saturation in relation to calcite is primarily achieved in the evaporative regime of waters, secondarily also by addition of Ca and the decreasing of partial pressure of CO₂. The partial pressure – pCO₂ in the soil air strongly decreases towards the surface, and when solutions become saturated to the calcite that is precipitated (Li *et al.* 2018). An ascending shift of CaCO₃ is possible in the case when groundwater gradually evaporates, or when there is a higher CO₂ pressure at the surface, comparing to the lower positions (result of microbial activity). These processes are responsible for the formation of carbonates near or

directly on the surface (Khadkikar *et al.* 1998, Knuteson *et al.* 1989, Miller *et al.* 1987). We encounter them in recent or past water-bearing horizons and in coastal zones (e.g., Butt *et al.* 1977, Carlisle *et al.* 1978, Semeniuk & Meagher 1981).

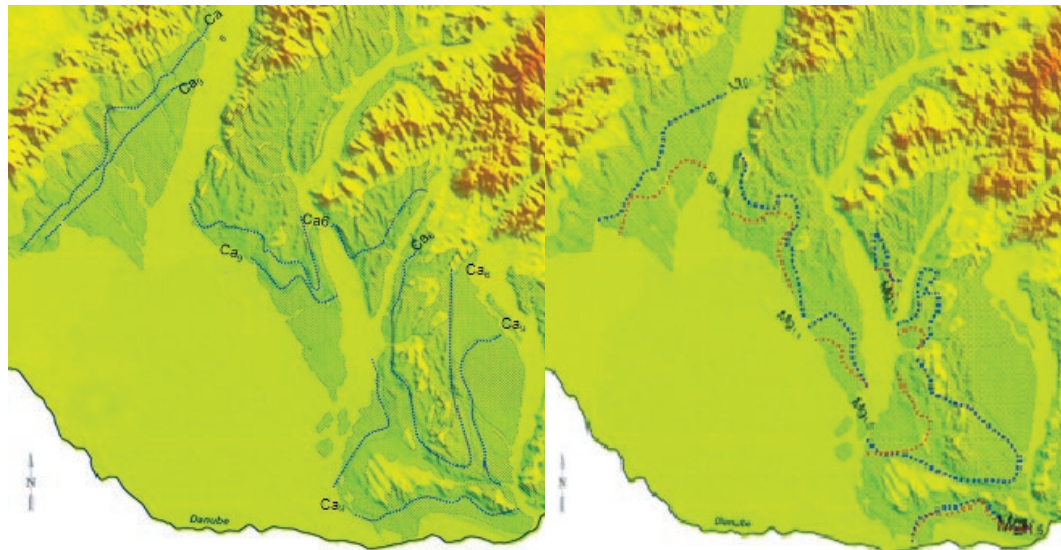
c) *In situ model* some authors connect with the local dissolution – precipitation of carbonates inherited from mother sources (e.g., Rabenhorst & Wilding 1986, Monger 2002). To this source, from in situ weathering of Ca – bearing silicate rock are added. For instance, in our older literature, we met the ideas that carbonates in loess come from feldspars weathering (Šajgalík & Motlidba 1983). But weathering and carbonates precipitation are two contradicting processes. Weathering of Ca-bearing silicate minerals is bound with intensive leaching and mobility of ions. Carbonates are weathered much more sooner as feldspars. Micromorphological study showed that in loess, together with newformed calcite, are occurred intact clastogene feldspars. Calcium from weathered feldspars may contribute only as additional non-substantial external source. Contents of Ca in such minerals are low, to produce higher amount of carbonates. Birkenland (1999) claims for this model additional atmospheric source of Ca. This model is the least reliable.

d) *Biogenic model* is based on ideas of possible carbonates formation by means of plants and microorganisms (biomineralization). Calcium as important nutrient is up taken by plants which bring it to the surface (Goudie 1973). Plants contain Ca-oxalates and new formed calcites, which after the plant decaying are accumulated in the soil (Franceschi & Nakata 2011, Monger 2002, Verrecchia & Verrecchia 1994, Cailleau *et al.* 2014). Ca concentration in plants depends on its content in the soil environment. It is documented that an increase in Ca contents in the soil environment is also reflected in increased Ca-oxalate contents in plant tissues (Franceschi & Nakata 2011). High contents of Ca and Mg in the soil, the presence of oxalo-morphic plants and high oxalo-trophic stability of microorganisms are prerequisites for the application of this model (Martin *et al.* 2001, Cailleau *et al.* 2014). In the loess and fluvial sediments of the Quaternary, gastropod shells are also often found. There are also data in the literature on the formation of calcite by biomineralization by the help of termites (Monger 2002, Verrecchia *et al.* 1994, Zamanian *et al.* 2016).

e) *The model of lateral transport of Ca* (and other ions) from source materials located on the slope was proposed and generally preferred by French soil scientists, for the formation of calcic horizons in places where surface and underlying soil horizons are unable to provide enough Ca. The movement of Ca takes place on the surface or at a certain depth below the surface of the soils (sediments), occasionally in the form of suspended particles. (Ruellan 1968, Reeves 1976, Elbersen 1982) also reported the transport of colloidal forms of CaCO₃, Monger (2002) explains the occurrence of calcretes by the lateral movement of solutions in different positions of the slope.

f) More recently, it was proposed by Li *et al.* (2018) *evapotranspiration model* as an extension of the ascending model. As water begins to evaporate from the exposed surface, the solutes migrate upward, or laterally, through the soil zone via capillary pores. These migration paths are the most conductive, and therefore, where the most concentrated CaCO₃ solutions is reached, the highest concentrations of authigenic carbonates can be observed. (Machette 1985, Li *et al.* 2018).

g) *In cascade types* of geochemical landscapes (which we will discuss in more detail below), *vertical* (ascending and descending) matter-energy flows are combined with lateral ones. A significant part of the precipitations that falls, runs off on the surface, or at some depth below the surface, with subsurface runoff reported, to be much more significant (Kirkby & Chorley 1967). With the lateral migration is connected a lateral differentiation of chemical elements and compounds in the landscape and the formation of *soil-geochemical catenas* (Genadijev & Kasimov 2004). In the lowest positions of super-aqual landscapes, concentrations of individual ions in solutions may also increase due to evaporative concentration. In such case the lateral migration flows in the landscape may change to the ascending flow. This is how lateral-geochemical zonality in the landscape is formed (Fig. 2) (Čurlík *et al.* 2011).



a) Calcium distribution pattern in loess
 Ca_6 – isoline of 6% content of Ca
 Ca_9 – isoline of 9% content of Ca
 b) Mg and Sr distribution pattern in loess
 $Mg_{1.5}$ – isoline of 1,5% of Mg content
 Sr_{150} – isoline of 150 mg of Sr content
 Figure 2. a, b) Areal distribution pattern of Ca, Mg (Sr) in loess, in the Danube Lowland.
 Note zonal character of chemical elements in the lowland (Čurlík 2005).

For these conditions we propose, as the most suitable, *the landscape-geochemical model* – the model that refers to the formation of authigenic carbonates.

Except those listed, there can be mentioned many combined models, the presence of which is more controlled by soil or more by groundwater (Chen *et al.* 2002). Most often, individual models are combined. For example, the *per ascendum* model, which is associated with the formation of carbonates under the influence of groundwater, can be combined with the *biogenic* and *evapotranspiration* model if the groundwater lies close to the surface.

The *per descendum* model can be combined with the model of *lateral* movement of calcium. Some authors even merge these two models. On the contrary, the *evaporation of groundwater* in the capillary zone can be replaced by the *downward movement* of substances, when the climate and relief change, especially in subhumid conditions. The lateral (subhorizontal) movement of water on slopes can result in an upward movement in the super-aqual part of the landscape, especially in places with a significant evapotranspiration regime. Individual operation of any of the models is rare. If so, it reflects the special conditions in the host materials. Some models can also have an episodic character linked to a certain time-space section of development.

Carbonate geochemical systems of cover sediments and soils of the Danube Lowland

Each geochemical system is characterized by three main attributes: a) mutual relations between the components that create the system, b) the response of the system to environmental changes, c) the history of the changes that took place in the system (Alexejenko & Alexejenko 2013). Carbonate geochemical systems of the supergene zone differ from other geochemical systems by the concentration of calcium, or the presence of the paragne association of elements that form accumulations of authigenic carbonates in the host materials. In the geochemical landscape, they represent a continuum mutually connected through the one-way migration of elements.

The development of cover sediments (and soils) as carbonate geochemical systems is determined by the action of various flows of matter and energy (information). Besides the vertical flows, lateral (sub-horizontal) flows on- and under the surface (sediments and soils) must also be considered. Flows of matter and energy take place in the gravitational field, which determines the direction and intensity of migra-

tion. Individual matter-energy flows have changed historically, just as the external conditions in the system.

The contents of CaCO_3 , which is excreted in host materials such as loess, weathering crusts, sediments and alluvial soils are variable and vary from a few to almost 100%. The distribution of individual forms of carbonates with depth, their shape and size, as it follows from the microscopic study indicates, that during historical development, the water regime played a decisive role in their spatial distribution.

The most important carbonate systems of the Danube Lowland include: 1) loess and 2) carbonate alluvial sediments. They are cascade types of geochemical systems characteristic by one-way flows of matters, energies, and information (Gennadijev & Kasimov 2004). An essential factor in their formation is sufficiently high concentrations of calcium (Mg, Sr, Mn, Fe, Na) in pore – and groundwater and suitable climatic conditions, that affect water evaporation (evapotranspiration regime). In both systems, there is a variable ratio of chemical elements, different forms, and ways of their migration, as well as different geochemical barriers on which these elements are deposited. Loess is older and its development is linked to aeolian processes and to the forest-steppe or meadow-steppe systems of the Pleistocene. Alluvial sediments are younger, and their development is linked to the alluvial activity of streams, rivers and super-aqual systems of the Pleistocene and Holocene. Unlike loess, where geochemical flows are mediated by precipitation, in alluvial sediments matter-energy flows, are also provided by groundwater. The alluvial systems and especially the soil cover is mostly Holocene. The geochemical junction and interconnection of these systems is determined by lateral water migration (Chorley & Kennedy 1971). The formation of both systems was accompanied by the oscillations of external environmental conditions (climate), which are reflected in the spatial differentiation of the chemical composition of each system.

Loess as carbonate systems – historical aspects

Loess is relatively homogeneous, macroporous sediment. It is composed mainly of silty particles weakly cemented with Ca-carbonates. In common works on Quaternary sediments, loess is considered as a simple aeolian sediment. That's an oversimplification. Aeolian origin has only the dust. Atmospheric dust cannot turn into loess in every geographic environment. The part of aeolian dust that is deposited in special geographical (ecological) conditions (dry, cold, periglacial climate or dry desert climate) becomes loess only after a certain time, as a result of epigenetic (post-sedimentary) changes of the so-called “loessification”. Loessification is a term used by many authors to denote quasi-pedogenic/quasi-diage-

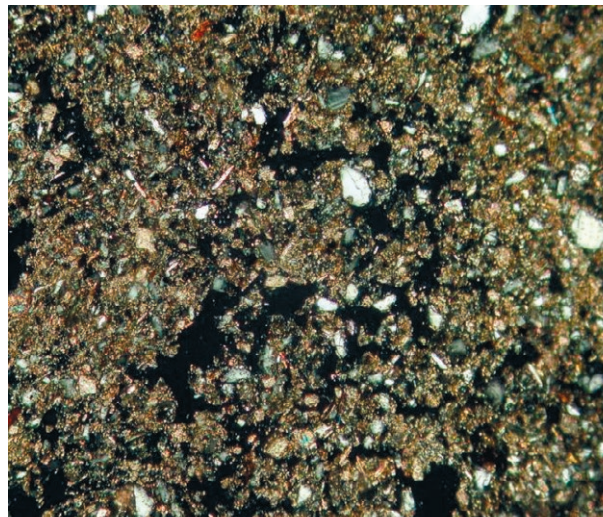


Figure 3. The fabric of typical loess under the polarising microscope on Trnava Hilly land. Note the high porosity and the fine powdery groundmass and with fine micritic calcites (cross polar. magn. 28×).

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netic process, the result of which is the creation of a porous texture of silty sediment and the formation of carbonate nature (Fig. 3) (Berg 1964, Ložek 1965, Pécsi 1990, Perelman & Kasimov 1999). The conditions of loessification are in arid to semi-arid climate, which is characteristic of steppes, deserts, and semi-deserts, i.e., countries characterized by low humidity, low average precipitation (between 200 and 600 mm) and relatively rapid water evaporation (evaporative water regime in the landscape). Currently, many authors are inclined to the opinion about loess formation by loessification (Arkley 1963, James 1972, Goudie 1973, 1983, Hay & Reeder 1978, Wright & Tucker 1991, Pécsi 1990, Lal *et al.* 2000, Gocke *et al.* 2012, Smalley & Obreht 2018, Li *et al.* 2018, Gaita 2020).

Our microscopic study has also proved this theory (Fig. 4).

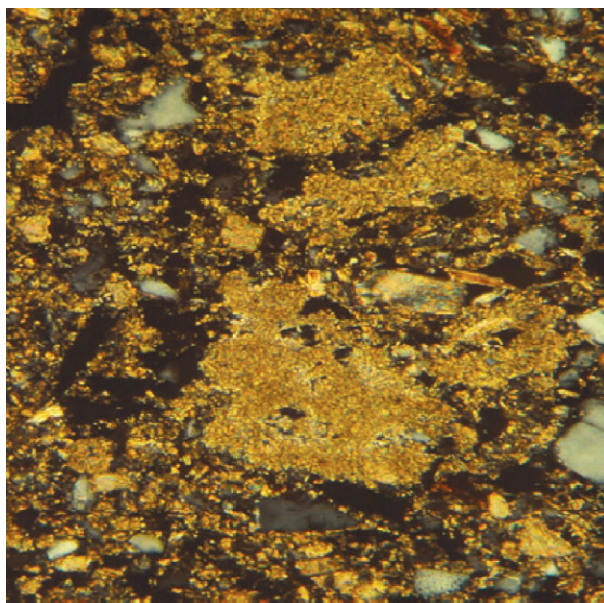


Figure 4. Clusters of micritic nodules of authigenic calcites in the loess matrix. (A typical sign of loessification). Besides authigenic, also clastic calcites are presented (blue rhomboeders point to particles of clastogene calcites in the matrix); cross polar. magn. 62×).

Different opinions also concern the formation of authigenic (secondary) carbonates in loess, as component part of loessification. Authigenic carbonates are formed in arid and semiarid conditions, where water deficit inhibits leaching and favours the precipitation of carbonates. Calcium and other ions (Mg, K, P, Na, Sr, etc.) necessary for the formation of carbonates in loess (as subaerial sediments) come from dry and wet atmospheric depositions (rainfall, dust, aerosols), from abiotic and biotic dissolution (weathering) of carbonate and silicate minerals (Capo & Chadwick 1999, Čurlík 1985), from animal shells and plant fragments, as well as from the transfer of calcium (Ca and HCO_3 ions in solution) in the landscape, from surrounding sources rich in carbonates (Perelman & Kasimov 1999, Chen *et al.* 2002, Monger 2002). According to Glazovskaja (1965), in the conditions of steppes and deserts, where loess is formed, 15–18 t of $\text{CaHCO}_3 / \text{km}^2 \cdot \text{yr}^{-1}$ is received by atmospheric precipitation, which can be transformed by microorganisms into calcite.

Gile *et al.* (1966) reported that carbonates from precipitation exceed two to three times the amounts brought by dust. Bockheim & Douglass (2006) link the formation of authigenic (pedogenic, secondary) carbonates in loess with the alteration of silt fraction of clastic carbonates. Barta (2014) stated that “secondary carbonates in loess are formed during vertical, horizontal, or in situ rearrangement of carbonates during pedogenesis in the soil-sedimentary environment”. Some authors stated two types of carbonates in

loess: *primary* – detrital and *secondary* – products of dissolution-migration-recrystallization of primary carbonates, during loess development (Smalley & Marković 2014, Li *et al.* 2018). On the contrary, Pye (1995) admits a certain modification of an aeolian dust by local reworking, bioturbation, and syn-sedimentary weathering, but epigenetic changes – loessification is not for him a precondition to name it loess. He defined loess as “*terrestrial, clastic, powdery sediment, that is formed by the accumulation of an aeolian dust*”. He considered that carbonates present in the loess are mostly clastogene. This opinion is rather exceptional and perhaps refers to the conditions of loess formation in Western and Northern Europe. If we accept the thesis of Pye (1995), on the occurrence of only clastic carbonates in the loess, it would be necessary to explain where calcium (and accompanying ions) is lost from precipitation in arid climatic conditions. We also do not agree with the view presented by Mush (2007) that “*primary loess*” contains only primary (clastogenic) forms of carbonates. This definition ignores the opinions of many authors, as well as our knowledge, that in places where primary carbonates are preserved, there are also conditions ready for the formation of authigenic (secondary) carbonates. The loess itself is easily erodible, and its mineral components may again be subject to loessification after the relocation. In practical observation, traces of loess redeposition are often not recognizable due to the similar nature of post-depositional processes, both, in primary and relocated loess. In relocated loess, the same minerals, as in primary loess are preserved, along with newly acquired features and fabric. On the Nitra and Hron loess hilly lands, for example, we identified secondary loess under the microscope, based on the presence of litho-relicts of the underlying Neogene claystones in groundmass, and on the basis of the multigeneration nature of nodular forms of authigenic carbonates (Čurlík 1996) (Fig. 5).

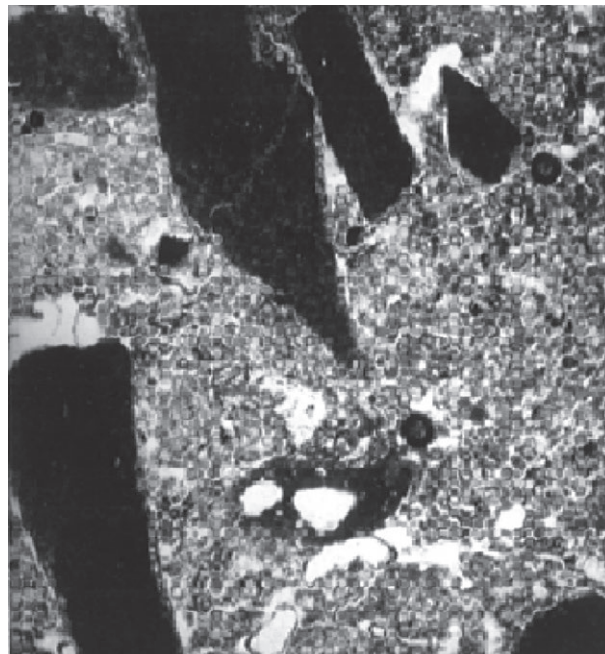


Figure 5. Lithorelicts of Neogene claystones (black), in a secondary (relocated) loess on the Hron Loess hilly land (polar., magn. 28×).

The genesis of loess remains a controversial and debated topic, in geological, pedological and geographical literature. Misunderstandings on the loess genesis are the result of a dual approach to their study. Soil scientists understand loessification as part of soil-forming processes. Loess contains bio-pores, channels along the roots, stems of plants, humus (0.3–0.8%), similar to the humus of desert soils and signs of the aggregation. From this point of view, loess is perceived not only as an aeolian sediment but also as soil, while dust sedimentation and pedogenesis is considered syngenetic processes (Perelman & Kasimov

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1999). At other times, they consider loess as the parent material, or as the C horizon of the soil. For example, Barta (2011) has reported that „during the accumulation of loess, pedogenesis is not completely interrupted, but strongly inhibited by the higher sedimentation rate of the loess”. Pécsi (1990) as a supporter of loess formation by loessification stated that loess is formed only in places where the rate of dust accumulation is greater than surface washout, or pedogenesis (weathering). He defined loess as “a loose sediment, with a predominance of the dust fraction, non-stratified, porous, permeable, stable at vertical walls, easily erodible by water, loamy, pale ocher – due to finely dispersed limonite, containing quartz as the main mineral component (40–80%), less feldspars, with a variable content of clay minerals (5–20%) and carbonates (1–20%). It follows, that the rate of dust accumulation in an arid environment is primarily the most important factor of the loess formation, since at lower rate, the dust would be transformed into a soil (or, when strong weathering, into loam and clay).

Geologists rightly consider loess as aeolian sediments and loessification as the first stage of diagenesis. Accumulation of thick dust deposits usually requires long-term tectonic, climatic, and hydrological stability of the landscape. Thick accumulations of an aeolian dust are sufficient to define loess as a sedimentary formation, similar to aeolian sands, sandy loess, carbonate fluvial sediments and the like. Dust accumulation is not a pedogenic process. Without an aeolian dust accumulation (sediment genesis) there would be no loess. On the other hand, diagenetic transformations of dust (loessification), associated with the formation of authigenic carbonates and stabilization of the fabric, does not need to be associated with pedogenic processes.

According to some authors, the formation of authigenic carbonates is caused by “hydrogeochemical” reactions after the deposition of aeolian dust (Smalley & Marković 2014). Post-aeolian-geochemical processes are necessary to create the fabric and some loess properties (collapse, tunnel erosion). In the literature, they are referred to, as “*petit loessification*” (Smalley & Marković 2014). The discussion on loess environment formation (desert versus glacial and mountainous loess) is quite extensive and intuitive. Some authors report that both glacial and desert loess participate in the vast area of Chinese loess (Liu *et al.* 1985). Due to the geographical position, this discussion has no greater significance in the conditions of the Western Carpathians, although desert dust from the Sahara occurs frequently in these regions.

The supersaturation of the solutions necessary for the precipitation of carbonates can occur due to: 1) a decrease in the water content in seepage solutions (evaporation) (Arkley 1963, Gocke *et al.* 2012), (2) changes in pH values (Wen 1989, Li *et al.* 2018), (3) reductions in the partial pressure of CO₂ (pCO₂) in the soil air with depth, 4) Ca-uptake by plants and biomineralization (Čurlík 2014). However, water evaporation is primarily the most important factor (Arkley 1963, Gocke *et al.* 2012). It occurs in places with an evaporative water regime. There, the pore solutions evaporate back to the surface and leave a proportion of salts (evaporative concentration of elements (Perelman 1975). The uptake of Ca by plants and biomineralization can also be of great importance for the formation of loess, as well as for the preservation of the carbonate nature of soils (Čurlík 2014).

The loess was formed during the glacial periods of the Pleistocene. In the Danube Lowland these periods were associated with many climatic oscillations associated with erosion, slope modelling and relocation of loess (Šajgalík & Motlidba 1983). Climate fluctuations were mainly manifested by alternating cold-glacial and warm-interglacial periods. Glacial periods lasted 100–120 thousand years, interglacial approximately 10,000 years ($\pm 2,000$). For the last 800 thousand years four glacial periods (Cromer, Elster, Saal and Weichsel) and 11 interglacial periods were recorded. During the glacial periods, there was no permanent glaciation in the Danube Lowland, there was no tundra, but a loess steppe. The average annual temperatures were below freezing point, but the summer was warm. The area of Central European loess was therefore permanently revived, and biota also took part in shaping of loess properties (Kukla 1978, Ložek 2010).

In the area of the Danube Lowland, loess covers around 3,000 km². It forms continuous covers on the Trnava, Nitra, Žitava and Hron loess hilly land, on the river terrace steps and discontinuous, also on the Ipel loess hilly land. Their characteristic feature is their powdery nature (predominant fraction 0.05–0.63

mm), macro-porous texture and carbonates content. The loess of the Danube Lowland shows significant variations in thickness, grain size and geochemical composition on individual hilly lands. They reach an average thickness of 6 m, but locally exceed 10 m (Šajgalík & Motlitba 1983). Most of the loess covers that appear on the current surfaces of the hilly land of the Danube Lowland belong to Pleniglacial to Late Glacial sediments, younger than the Denenkamp Interstadial (Lower Visconian). Their age was determined, based on the fossil soils dating, on 23–21 thousand years (BP). It was the period in which the strongest cooling occurred (last glacial between 27–16 thousand years, with a maximum between 20–18 thousand years BP). According to some authors, the materials for the formation of loess were derived from moraine embankment dams, transported through the Moravian Gate, derived from weathered flysch and other rocks of the Carpathian Arc (Smalley & Leach 1978).

According to opinions of several authors, this young Pleistocene loess belong to the so-called Pannonian province (Vašková 1984, Šajgalík & Motlitba 1983, Frechen *et al.* 2003). Older loess (Mindel, Riss) was mostly eroded, relocated, or buried under younger covers, and it can be only found in vertical sections. Loess overlies pre-existing landforms, with the strongest accumulations in depressions or on broad, flat surfaces of loess hilly land. A micromorphological study of loess on the hilly land of the Danube Lowland confirmed a significant predominance of various authigenic forms of carbonates (Čurlík & Mejeed 1996). The groundmass consists of micritic forms dispersed in the matrix. There are also needle-shaped, nodular, rhizo-concretionary, and other forms (Čurlík 1993, Kolesár & Čurlík 2015, Čurlík & Kromka 2022).

In the older loess we find micro-sparitic domains of calcite, which coats clastogenic mineral grains. According to Brewer (1964), those “*crystallaria*” were formed by the recrystallization of micritic forms of carbonates during loess aging, which was also confirmed by our observations (Čurlík 1993). Those (crystic fabrics – Stoops *et al.* 2010), are clear evidence of the presence of authigenic forms of carbonates in loess. Clastogene (fragmentary, primary, lithogenic) carbonates are rounded similarly to other dust particles, they can be distinguished under a microscope according to microstructural features (shape, lamellation, newly formed calcite rims, micro-sparites) and are usually evenly dispersed in the matrix. They are present in the loess of the Danube Lowland, but their contents nowhere exceed the contents of authigenic carbonates.

The results of our studies show that the dominant mineral of authigenic carbonates in loess is *low-magnesium calcite*. We also recorded the co-occurrence of dolomite (by x-ray), but its authigenic origin was not reliably proven. Dolomite, which weathers powdery, dissolves more poorly than calcite. It is possible that clastogenic (primary) dolomite is incorporated into the matrix of authigenic calcites, which makes its X-ray study more difficult (Čurlík 1993, Čurlík & Mejeed 1996). According to data from the literature, stoichiometric dolomite does not even form under similar conditions, and data on the presence of dolomite in loess found in the literature refer to proto-dolomite, which contains up to 10 mol % more CaCO₃ (Degens 1965, Folk 1974). We make this assumption also because there is a higher proportion of magnesium in the loess in the Trnava hills, which reflects the presence of dolomite. This could have been generated from the Mesozoic of the Little Carpathians, where dolomitic rocks are often present. Microscopic study of loess also revealed the presence of Ca-oxalates and calcite in humified plant residues (Čurlík 1993, Čurlík 2014).

The designations “primary” and “secondary” loess distinguish those typically aeolian, from relocated (eroded) loess (Pécsi 1990). In practical observation, traces of loess relocation are often not recognizable due to the similar nature of post-depositional processes. In relocated loess, the same minerals as in primary loess are preserved, along with newly acquired features and microstructure, both in primary and relocated loess. On the Nitra and Hron loess hilly land, for example, we identified secondary loess under the microscope based on the presence of litho-relicts of the underlying Neogene claystone and based on the multigenerational nature of nodular forms of authigenic carbonates (Čurlík 1996).

According to some authors, the formation of authigenic carbonates is caused by “hydrogeochemical” reactions after the deposition of aeolian dust (Smalley & Marković 2014). Post-aeolian-geochemical pro-

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cesses are necessary to create the microfabric and formation of some loess properties (e.g., collapse, tunnel erosion). There was mentioned as “*petit loessification*” (Smalley & Marković 2014).

Carbonate systems of alluvial plains in Danube Lowland

Carbonate systems of alluvial plains of Danube Lowland belong to the cascade geochemical systems, which are typical by the one-way matter-energy flows. These flows run in gravity fields from the higher to lower hypsometric levels. Geochemical connectivity in the landscape is mediated by lateral water migration of substances, which maintains the integrity of these systems (Chorley & Kennedy 1971). Due to fluvial activities of rivers a large amount of detrital material (including limestone and dolomite fragments) is brought into river basins. Groundwater, which is a transporting medium, brings also necessary (Ca^{2+} , Mg^{2+}) ions for authigenic carbonates formation. Passing through the solid phases of water bearing strata, groundwater became gradually more and more concentrated, and on the *evaporative geochemical* barriers, authigenic carbonates precipitated. The main reason of this precipitation is evaporation of soil or groundwater. In alluvial regions, where groundwater tables lie near to the surface evaporate, leaving easily or sparingly soluble salts. For the salt's precipitation at the soil surface, the so-called *critical level of groundwater* is necessary. It is a depth which allows the capillary rise of water to the surface. This depends on climate and on the mechanical composition of soil. In sandy soil, capillary rise does not exceed 1 m. In loamy soils, capillary rise may reach 3–7 m. Evaporation of soil water may reach 4–6 m. When groundwater is situated bellow 10 m, its participation in soil forming processes is unlikely (Perelman & Kasimov 1999).

From the point of view of hydrological-geomorphological and landscape – geochemical organization, carbonate systems of alluvial plains of Danube Lowland belong to two different subsystems: a) systems of alluvial plains of rivers Váh, Nitra Hron and tributaries b) alluvial plain of Žitný ostrov.

Systems of alluvial plains of rivers Váh, Nitra Hron and tributaries

Ca (Mg and other) ions released by the dissolution of Mesozoic carbonate rocks (of the Tatras, Fatras, Považský Inovec, Biele Karpaty and Malé Karpaty with the Klippen belts) are brought into the river basins (Váh, Nitra, Hron and their tributaries). At the same time, clastic fragments of limestone and dolomite are deposited and preserved in the evapotranspiration conditions of the Danube Plain. Lateral tributaries of the rivers bring the loess material of the hilly land to the floodplain areas of the Danube Lowland, which is another source of Ca and carbonates.

As a result of the evapotranspiration water regime in this part of the Danube Lowland (Tomlain *et al.* 2002), there are conditions for the precipitation of authigenic carbonates (groundwater calcretes) and the preservation of clastogene in fluvial sediments and soils. Therefore, carbonate sediments and soils can be found practically throughout the whole Danube Plain. Detrital material transported by the activity of lowland rivers sedimented in floodplains, in riverbeds, on the sides of river valleys, on alluvial plateaus, alluvial cones and on the river terraces of the Danube Lowland. These are variable lithofacies, spatially changing formations, where gravelly, sandy to clayey loams and displaced loess alternate. The surface structure of the alluvial floodplains, which have the largest surface area, are dominated by loose clays, sandy loams, loamy sands, sands and humus-clay sediments with a thickness of 1 to 4 m. The content of the gravelly-stony skeleton in the sediments usually increases with depth. In the floodplains of individual rivers, we can observe the refinement of material in the lateral direction from the current riverbed to the marginal parts of the floodplains, as well as the gradual refinement of sediments in the direction of the flow of lowland rivers, linked to changes in the intensity of the hydrodynamic flow regime. In depressions and in abandoned dead river branches, bog peats were formed locally (Jurský Šúr, Modranský Šúr, Pusté Uľany, Hájske, and others). In the lowest lying (super-aqual) alluvial systems, the concentrations of Ca (Mg) ions in groundwater may have increased due to the evaporative regime. We refer to them as *cumulative concentrations of elements*. In fluvial sediments and soils, authigenic carbonates could have been excreted from these waters.

The importance of the cumulative concentration of calcium in groundwater is pointed out by the river Hron floodplain, which is a part of the geomorphological subdivision of the Danube Hilly Land. River

Hron, which drains crystalline rocks and Central Slovakian neo-volcanics does not bring as much dissolved calcium and carbonate clasts as rivers Váh, Nitra and their tributaries. The soils developed on these alluvial sediments are not carbonate in nature. Carbonates of an authigenic nature are secreted there only locally in the lower course of the river, in the lower soil horizons, in the zones of capillary rising groundwater and in places where loess from the adjacent Hron Hilly Land was redeposited.

Alluvial plain of Žitný ostrov as geochemical system

Žitný ostrov is a region that stretches between the Danube and the Little Danube (intracontinental Danube delta: 1885 km², SW Slovakia). It is part of the geomorphological unit of Danube plain the area of Danube Lowland, sub-province of the Little Danube Basin, the province of the West Pannonian Basin. (Mazúr & Lukniš 1978). It is the largest river island in Europe. It represents a carbonate geochemical system, which has a special character conditioned by groups of a) geological, b) hydrogeochemical and c) climatic factors (Čurlík & Dlapa 1994, Fulajtár *et al.* 1988, Čurlík 2005).

a) It is a low-lying, young structural river plain, slightly inclined to the SE (Bratislava 134 m, Dunajská Streda 118–119 m, Komárno 108 m a.s.l.). This sloping was created by the gradual gravel, sand, and mud deposits. Slight sloping makes difficult for water to drain (Mazúr & Lukniš 1978). Unlike the alluvial plains of Slovak rivers, Žitný ostrov is built by sediments brought by the Danube from Alps. From a geological-morphological point of view, it is important to note that roughly from Mindel, the development of basin was running in no river-lake conditions. The Danube meandered strongly and practically branched from the Little Danube to the Mošon branch of the Danube. Basin continued to develop with syn-sedimentary subsidence. The river network supported the deposition of huge gravelly and sandy sediments, the thickness of which reaches in depressions up to 400–450 m. The branching Danube was able to fill with the sediments, the relatively decreasing territory, and even created a massive alluvial cone, surpassing the surrounding terrain, along the top of which it also mostly flowed. The most pronounced elevation (Middle and Upper Pleistocene) comprised by thick sandy gravels of the middle fluvial and bottom formation and goes through the centre of Žitný ostrov. It represents the morphologically oldest and driest part. Pleistocene gravel-sand sediments are overlain by Holocene fluvial sediments, in which sandy to clay loams, occasionally with an admixture of gravel, recent and fossil soils alternate. They represent the floodplain alluvial cover of the Danube.

b) The Danube, our largest river, drains the carbonate mountains of the Eastern Alps. As an alpine-type river, it has the highest water levels at the beginning of summer (May-June) when the snow in the Alps melts. On the other time, air temperatures on Žitný ostrov are already high, which supports the evapotranspiration water regime. The groundwater of Žitný ostrov is supplied by the Danube. The water is Ca²⁺, (Mg²⁺), HCO₃⁻ weakly alkaline, low mineralized moves sub-parallelly with Danube water (SE). The gravel sand formation contains one of the largest groundwater reservoirs in Central Europe (around 10 billion m³ of reserves). Due to interaction with solid phases of aquifer horizons, groundwater is enriched with many substances, transporting them in the landscape they and could be deposited in another place depending on hydrogeological conditions. Passing through the solid phases of aquifer horizons of weakly alkaline, low mineralized groundwater, become more mineralized (locally above 1000 mg/l) in the lower Žitný ostrov. Gradually different hydrogeochemical zones are formed (Čurlík 1993). Groundwater contains 800–2200 mg/l of dissolved substances, around 180–870 mg/l of sulphates, 40–50 mg/l of chlorides, 15–170 mg/l of nitrates, 160–250 mg/l of calcium, 40–50 mg/l magnesium, up to 90 mg/l sodium, up to 10 mg/l potassium and up to 1.3 mg/l iron (DANREG, Pristaš 2006). Currently, there has been a drop in the bottom and water level in the Danube and changes in the of groundwater level along the entire length of the island.

c) The region belongs to a warm, moderately dry to dry climate zone characterized by an evaporitic water regime. The average annual precipitation is low (590 mm). Potential evaporation (according to Tomlain 1980) is around 800 mm per year. The average difference between evaporation and precipitation potential in summer is 340–345 mm. The most precipitation is in winter. The number of summer days with a maximum temperature above 25 °C is more than 50 days (more than 60 near Bratislava and more

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than 70 in the SE part of Žitný ostrov. The average annual temperature is 9 °C. Thanks to the mentioned factors, some common features have been preserved in the soils: all soils have an alkaline reaction, carbonate nature, different content of clastogenic and authigenic forms of carbonates. In these conditions a special geochemical structure of the soils of Žitný ostrov area was developed (Čurlík 2005). The nature of the lateral differentiation of elements in this landscape-geochemical system is related to the different hydromorphic influence of soils and sediments. Thanks to the soil memory, which we mentioned elsewhere, former soil characteristics are preserved in the morphology of recent soils. The contents of clastogenic carbonates are significantly higher than in the alluvium of other lowland rivers (Váh, Nitra, Hron), because the Danube brings carbonate detritus from the Austrian Alps. The share of clastogenic dolomite is also higher. The forms of authigenic carbonates (calcretes) in the soils and sediments are diverse (Čurlík & Mejeed 1996). Most often, they form a micritic cement dispersed in the soil matrix. Carbonates are often found as coatings and pore infillings, micro-sparitic crystals, calcified plant roots. Large accretion forms, clusters, nodules, and layers of authigenic carbonates up to 20–30 cm thick (locally referred to, as “*atka*”) occur in the central part of the Žitný ostrov (Dolný Bar) (Fig. 6).

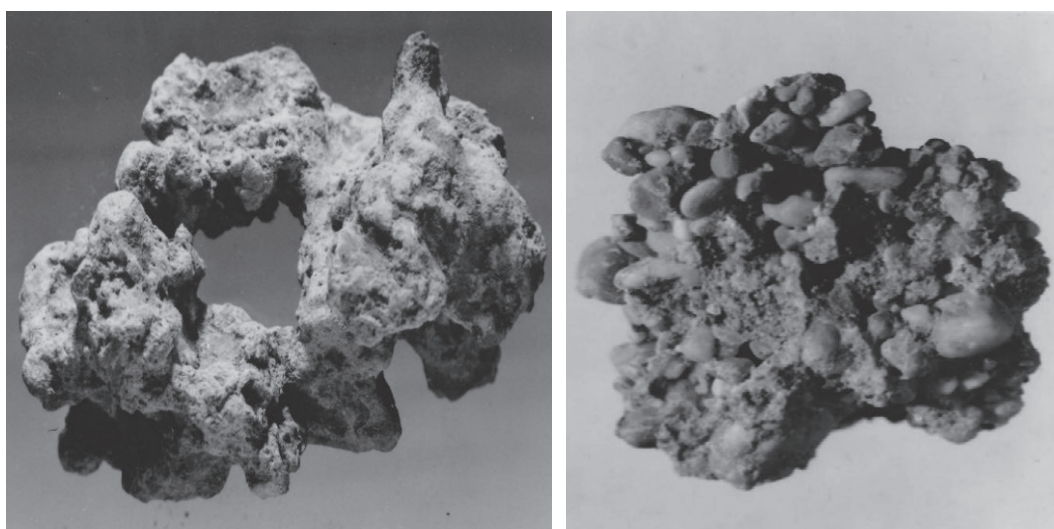


Figure 6. Groundwater calcretes in fluvial sediments of the Žitný ostrov (a) nodular forms, b) conglomeratic forms (fragment); about ¼ of original size)

Several meter-thick layers of pendant (gravity) cement on the bottom sites of the gravels are present in the core of Žitný ostrov. The cement has complicated layering as a result of sequential aggradation and shows incremental lines of speleothems. Speleothems are several mm thick, this cement was formed during the processes of descending decarbonatization, when the water percolating through the positions of the gravels stayed more (longer) on the lower side of the gravels (Stoops *et al.* 2010). The cement has a complicated layering because of sequential aggradation. Despite the transverse lamination, under the microscope, they appear as micro-sparitic (palisade) crystals. The formation of the cement is gradual. There are indications that micritic domains and needles were formed in the first phase, and transverse clusters of palisade crystals recrystallized only later (Fig. 7). In the gravels overburden there are Chernozems – carbonate soils up to the surface, which indicates that evaporitic condition was restored again in the Holocene.

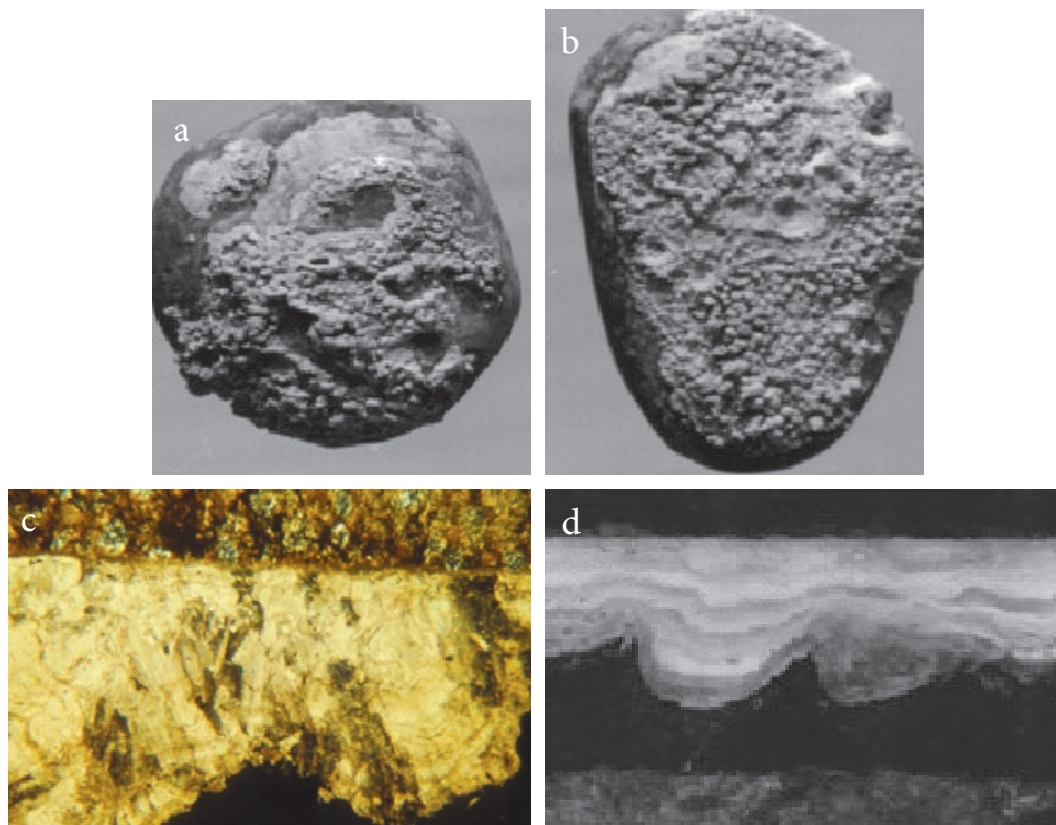


Figure 7) a) Cross section through the pendant cement speleothems on the gravels of Žitný ostrov; b) pendant cement on lower side of gravels; about 1/4 of original size; c) d) cross sections through the speleothems with differed forms

CONCLUSIONS

The most important carbonate systems of the Danube Lowland include: 1) *loess*, 2) *carbonate fluvial sediments*. They are cascade types of geochemical systems characteristic by one-way flows of matters, energies, (information).

The development of cover sediments and soils as *carbonatic geochemical systems* in Danube Lowland, is limited by the flow of matter and energy (information) in the conditions of evapo–transpiration water regime.

The carbonatic geochemical systems of the Danube Lowland differ from the other geochemical systems in the supergene zones by the concentration of calcium and the paragenetic association of chemical elements, that comprises authigenic carbonates in the host materials.

The carbonate authigenesis is epigenetic geochemical process which leads to the excretion (neof ormation) of carbonates in the host sediments and soils, independent on their genesis. It is applied on places where are sufficiently high contents of calcium in pore or groundwaters and suitable evapotranspiration landscape potential.

Loess as carbonate systems was formed by wind action, in glacial periods of Pleistocene. They cover preexisting landscape forms, with most thick accumulations in depressions, and on the broad flat surfaces of Danube Lowland Hilly land. They form continuous cover on Trnavská, Nitrianska, Žitavská and Hronská Hilly land, on river terraces and disjointed on Ipel' Hilly land.

Fluvial sediments as carbonatic systems are younger, mostly Holocene. The fluvial activity of lowland rivers brought soluble (Ca, Mg, Sr, Mn, Fe, Na)) ions and clastogenic calcareous materials to the floodplains of the rivers. An essential factor in their formation is sufficiently high concentrations of calcium in pore-

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and groundwater and suitable climatic conditions. These include two subsystems: floodplains of lowland rivers (Váh, Nitra, Hron) and Žitný ostrov (Danube).

In alluvial (super-aqual) areas, where groundwater levels are close to the surface, the water rises in the capillary systems, evaporates, leaving easily and sparingly dissolved salts in the soil. Critical depth of groundwater is the depth that allows the capillary rise of water to the surface, depending on the climate and the mechanical composition of the soils.

Superimposed soil forming processes had weaker or stronger impact on calcaric parent materials (loess and fluvial deposits) to their nature. They disturbed microstructure of authigenic carbonates (decalcification), caused humus degradation, dispergation and a translocation of colloids, depending on the relief and climate conditions.

Due to the redistribution of substances on the loess hills of Danube Lowland, as postdepositional changes of loess, soil – geochemical zonality was created.

With the gradual changes of groundwater mineralisation, in this super-aqual landscape different hydrogeochemical zones are formed. Chemical element which migrated in groundwater were redistributed in the solid phases of aquifers.

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